

SOLVENT EXTRACTION PROCESS DEVELOPMENT FOR PARTITIONING AND TRANSMUTATION OF SPENT FUEL

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Abstract

Argonne National Laboratory (ANL), along with other national laboratories, has been developing a solvent extraction process for partitioning of spent fuel constituents to lead to safer and cheaper disposal of high-level waste. The process, known as UREX+, separates key radionuclides from dissolved spent fuel into: (1) uranium for disposal as LLW, (2) technetium for disposal as HLW, (3) iodine for disposal as HLW, (4) Cs/Sr for decay storage followed by disposal as LLW, (5) Pu/Np for production of mixed-oxide fuel, (6) Am/Cm for fast-reactor fuel or transmutation, and (7) all remaining soluble fission products for disposal. This paper discusses the ANL development effort including (1) design of process flowsheets by data collection and flowsheet development using the Argonne Model for Universal Solvent Extraction (AMUSE) code, (2) design of an advanced ANL centrifugal contactor, and (3) demonstration of alternative solvent extraction flowsheet options for the UREX+ process using dissolved fuel.

Introduction

The Advanced Fuel Cycle Initiative (AFCI), funded by the U.S. Department of Energy's Office of Nuclear Energy, Science and Technology, is developing advanced technologies to safely and economically reduce the volume and heat generation of material requiring geologic disposition, thereby extending the capacity of the Yucca Mountain repository and delaying or avoiding the need for a second repository. An important element of this initiative is the separation of key radionuclides followed by their incorporation into superior waste-disposal forms and/or transmutation of long-lived isotopes. To that end, the AFCI is developing advanced fuel reprocessing systems that separate key radionuclides from spent fuel. One of these systems is the UREX+ process.

The UREX+ process is being developed by Argonne National Laboratory (ANL) and other DOE national laboratories [1]. During Fiscal Years 2003 and 2004, two alternative UREX+ solvent extraction processes were demonstrated using multistage, countercurrent centrifugal contactors in ANL's Chemical Engineering Division. Three multistage 2-cm centrifugal contactors were used for this demonstration — one unit located in a shielded cell, a second in a glovebox, and a third in a vacuum-frame hood. The feed consisted of actual spent fuel that had been dissolved in nitric acid. A pin of irradiated Big Rock Point uranium oxide fuel was dissolved in nitric acid at elevated temperature and pressure. The composition of the fuel pin was calculated, using the ORIGEN2 code, from the initial pin composition and the known and assumed operating parameters of the Big Rock Point boiling water reactor. In preparation for dissolution, the fuel pin was chopped into 3- to 5-cm segments, and detailed chemical analysis was conducted.

The flowsheets for each UREX+ process segment were developed using the Argonne Model for Universal Solvent Extraction (AMUSE) code. AMUSE is an updated version of the Generic TRUEX Model (GTM) that was developed during the 1980s to design multistage countercurrent flowsheets for the TRUEX solvent extraction process [2,3]. GTM and AMUSE are developed to give highly accurate predictions of chemical behavior in a solvent extraction process by calculating component distribution ratios using chemically correct equilibria and thermodynamic activities for the major components: hydrogen ion, nitrate, and water. Further, the countercurrent mass balance algorithm contains terms for stage efficiency and other-phase carryover for both the aqueous and organic phases. The UREX+ process flowsheets were designed for the number of stages available for use and therefore were not optimized for plant-scale processes.

Data collection and flowsheet development in the AMUSE code for design of process flowsheets

The AMUSE code is composed of two major sections, SASSE and SASPE, which interact and are executed by Microsoft Excel software. SASSE, or Spreadsheet Algorithm for Stagewise Solvent Extraction, calculates multistage countercurrent flowsheets based on the distribution ratios calculated in SASPE (Spreadsheet Algorithm for Speciation and Partitioning Equilibria). Figure 1 illustrates the relationship between the two sections and the user inputs that are required for both sections.

The SASPE section calculates distribution ratios based on the input compositions and conditions of the aqueous and organic phases. The accuracy of the SASPE D-value calculations over a wide range of aqueous phase compositions is due to chemically correct models that use the thermodynamic activities of the major aqueous-phase species. These activities are calculated in SASPE from aqueous-phase compositions using the approach of Bromley [4].

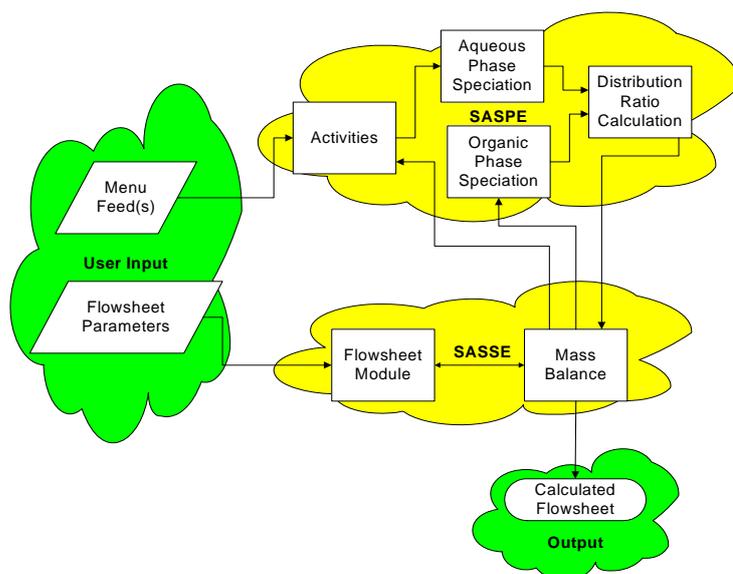


Figure 1. Simple schematic of AMUSE operations data.

The water activities (a_w^0) of single-component electrolytes are calculated from their osmotic coefficients, which are in turn calculated using an expanded Debye-Huckel formula modified to fit experimental data for specific salts. Water activities of mixed electrolytes are then estimated from single-component activities and molal concentrations using Meissner's method. Solvent loading is calculated using the distribution ratios calculated in SASPE, and the aqueous and organic compositions calculated in SASSE to calculate the concentration of free extractant in the solvent. Distribution ratios are then readjusted to account for the reduction in the amount of extractant that remains available for each extractable species.

When AMUSE is used to calculate flowsheets, the SASPE section of the model will calculate distribution ratio (D) values for each aqueous-phase composition from user-specified inputs and from stage compositions generated by SASSE. The SASSE section will then refine the calculated D -values based on the compositions calculated with SASPE. This iterative process continues until convergence is achieved. Figure 2 shows an example of how the experimentally determined D -values for Pu as a function of nitric acid composition [5] are used to determine the relationship necessary to predict the D -values calculated by AMUSE. Similar calculations are done for all feed components.

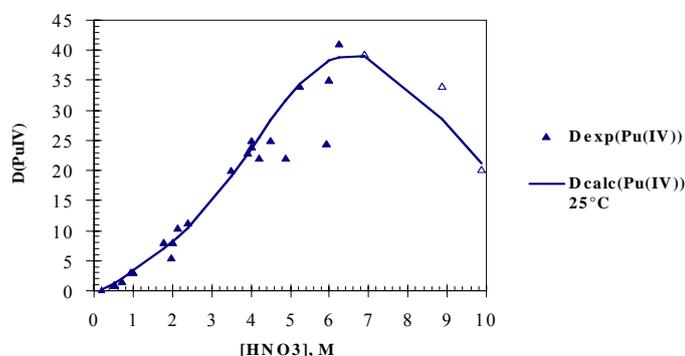


Figure 2. Experimental and calculated distribution ratios of Pu(IV) vs. nitric acid at 30% TBP, 25°C.

The SASSE section allows the design and detailed evaluation of proposed flowsheets in conjunction with distribution ratios generated in SASPE. SASSE can be used to (1) determine that each feed component will reach its design composition in the raffinate and product streams, (2) provide the compositions of the organic and aqueous solutions in each stage of the flowsheet at steady state, and (3) identify key points for process monitoring and control.

The user interface is composed of forms with input fields for information that is required before the program can be run, including equipment, section feed composition, and general flowsheet specifications (e.g., number of stages, temperature, flow rates). A sample input form is shown in Figure 3.

AMUSE will calculate a solvent extraction flowsheet based on input of a specified feed and a specified set of process goals. The output will include (1) compositions of all of the effluent streams, (2) compositions of both phases in each process stage at steady state in both graphical and tabular forms, (3) stage-wise D-values, and (4) a diagram of the final flowsheet. Other options are available to calculate the aqueous phase speciation, thermodynamic activities, and distribution ratios of extractable species.

Figure 3. A user input form in AMUSE.

AMUSE can readily calculate solvent extraction flowsheets for PUREX, UREX, SREX and TRUEX if feed compositions are known. With input of appropriate D-values, flowsheets for many other processes including CSSX, CCD-PEG, and TALSPEAK can be generated and evaluated.

In addition to generation of specific flowsheets, AMUSE can be used to determine the effect of process variations on a specific flowsheet. Sensitivity analysis can define the effects of flow rate variation, compositional variation, stage loss, other-phase carryover, temperature excursions, and equipment type. As an example, AMUSE was used to evaluate possible causes of deviations between the product compositions calculated by AMUSE and the results from a demonstration of the UREX process at Savannah River Technology Center (now Savannah River National Laboratory) [6] with spent nuclear fuel. Using AMUSE to look at variations in flow rate, feed composition, process efficiency, and temperature, we were able to better gauge the relative contributions of these different parameters to the differences between the expected and observed results.

One of the factors studied was the effect of temperature on product composition. The process flowsheet was developed using AMUSE, assuming an isothermal process; however, a non-isothermal temperature profile was observed experimentally. AMUSE was used to evaluate the effect of operating temperature on product composition. Figure 4 shows the effect of temperature on the uranium concentration in the technetium product for several clean solvent flow rates to the technetium strip section [7]. Control of the process temperature becomes increasingly important as the solvent flow rate decreases. The effect of another variable, stage efficiency is shown in Figure 5. Poor stage efficiencies would have had a stronger effect on the concentration of uranium than technetium in the raffinate under the conditions of the test.

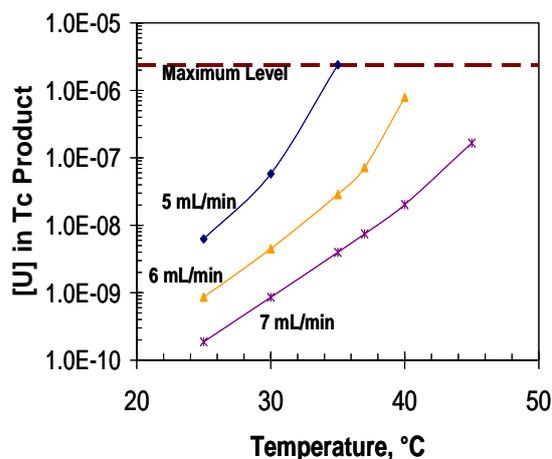


Figure 4. Effect of temperature on the concentration of U in the Tc product for three different Tc-strip solvent flow rates in the UREX process based on AMUSE simulations.

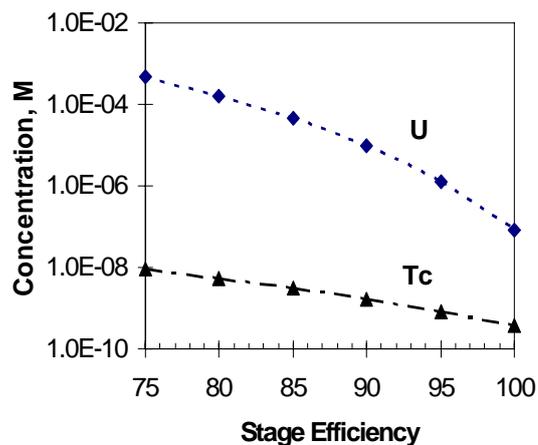


Figure 5. Effect of stage efficiencies on the U and Tc concentrations in raffinate of UREX process based on AMUSE simulations.

More recently, we have used AMUSE to develop flowsheets for the UREX+ [7] and UREX+2 processes to demonstrate the treatment of spent nuclear fuel as part of the Advanced Fuel Cycle Initiative. For the demonstration, these flowsheets consisted of a number of solvent extraction processes run in three centrifugal contactor banks. AMUSE was used to optimize flowsheets to meet product purity requirements while constraining the processes to the available equipment. In some cases sensitivity analyses were done using AMUSE to refine the processes to achieve desired results.

Design of advanced separation equipment – ANL centrifugal contactor

The annular centrifugal contactor was developed at Argonne National Laboratory in the early 1970s for carrying out solvent extraction operations required in the nuclear industry [8]. In stagewise solvent extraction, two immiscible liquids are contacted and then separated at each stage. For continuous countercurrent operation, the immiscible liquids must move in opposite directions as they flow from stage to stage. The schematic of a contactor stage in Figure 6 shows where the more-dense phase (typically the aqueous phase) and the less-dense phase (typically the organic phase) enter and exit the unit. The entering immiscible liquids are mixed in the annular region outside the spinning rotor. The mixture is disengaged by the centrifugal force in the separating zone of the rotor. The separated liquids are then forced to move out separate rotor exits by the two rotor weirs (the upper weir for the more-dense phase, the lower weir for the less-dense phase), where they are captured by separate collector rings near the top of the contactor housing. The liquids then flow by gravity to the appropriate next stage. A motor (not shown) located above the rotor spins the rotor. Further discussion of contactor operation can be found elsewhere [8-12]. When used to carry out a typical solvent extraction flowsheet, the contactor consists of (1) multistage extraction and scrub sections that recover selected elements from the feed stream and (2) multistage strip and wash sections that separate those elements from each other and the solvent.

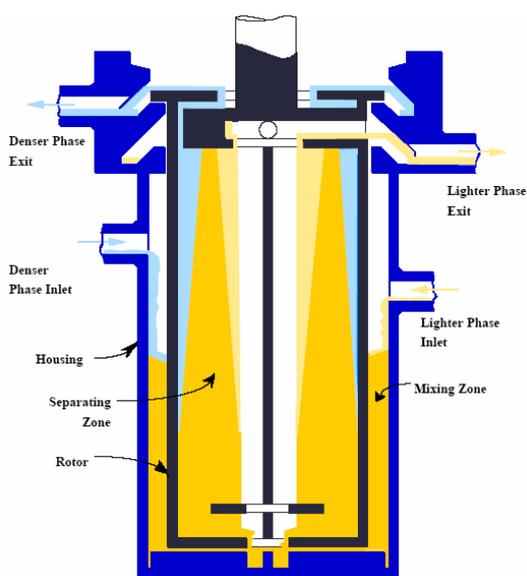


Figure 6. Schematic of operating contactor stage.

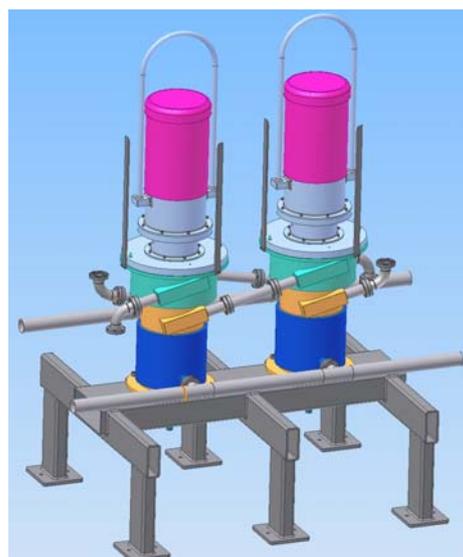


Figure 7. Prototype of a 2-stage 15-cm ANL centrifugal contactor unit.

In Fiscal Year 2004, a plant-scale contactor was designed for the AFCI program. The project criteria were (1) to design the contactor with the highest possible throughput while (2) still maintaining nuclear criticality safety for the various AFCI flowsheets. The new design features, based on established engineering practices, allowed the extension of contactor operation range. The contactor that met these criteria has a 15-cm rotor turning at 3600 rpm. The separating zone of the contactor rotor has a length-to-diameter (L/D) of 2.25. This 15-cm contactor has a nominal throughput of 40 L/min. Maximum flow rate could be as high as 60-80 L/min.

The design of the contactor was based on (1) 34 years of experience in building, testing, and using contactors at ANL; (2) a model for contactor operation developed at ANL; (3) experience in determining nuclear criticality safety at ANL; and (4) the latest drafting and mechanical design technology at ANL. The contactor design incorporates improvements developed at ANL over the years. It also has new features to provide ease of use and to allow remote maintenance during plant-scale operations in a canyon facility. A prototype of a 2-stage 15 cm ANL centrifugal contactor unit is shown in Figure 7.

Demonstration of alternative solvent extraction flowsheet options for the UREX+ process using dissolved fuel

During Fiscal Years (FYs) 2003 and 2004, two alternative solvent extraction processes were demonstrated using multistage, countercurrent centrifugal contactors in ANL's Chemical Engineering Division. Three multistage 2-cm centrifugal contactors were used for this demonstration—one unit located in a shielded cell, a second in a glovebox, and a third in a vacuum-frame hood. The feed consisted of Big Rock Point uranium oxide fuel that was dissolved in nitric acid at temperature and pressure. The composition of the fuel pin was calculated using the ORIGEN2 code with the following input: (1) burn-up of 29,600 MWd/MT, (2) initial enrichment of 4.6% ^{235}U , (3) 1% gadolinium burnable poison, and (4) cooling time of 21 years. Additional input was derived from the known and assumed operating parameters of the Big Rock Point boiling water reactor.

The UREX+ process flowsheet alternative demonstrated during FY03 consisted of a series of five solvent-extraction flowsheets that perform the following operations: (1) recovery of Tc and U (UREX), (2) recovery of Cs and Sr (CDC-PEG), (3) recovery of Pu and Np (NPEX), (4) recovery of Am, Cm, and rare-earth fission products (TRUEX), and finally (5) separation of Am and Cm from the rare earths (Cyanex 301). Details and results of the demonstration are given elsewhere [7,13].

During FY 2004, the UREX+2 process (an alternative to the FY 2003 flowsheet) was demonstrated. The UREX+2 process is a series of three solvent-extraction flowsheets and one ion exchange process that perform the following operations: (1) recovery of Pu, Np, Tc and U (co-extraction and ion exchange), (2) recovery of Cs and Sr (CCD-PEG), and (3) recovery of Am and Cm (TALSPEAK). The first two segments of the UREX+2 solvent extraction process, and the ion exchange process were demonstrated at the end of FY 2004. Each process was designed for $\geq 99\%$ recovery of fission products and $\geq 99.99\%$ for actinides. The flowsheets were developed using AMUSE; Figure 8 shows the process segments and streams that were run to co-extract and recover Pu, Np, U, and Tc. All of the processes were run in 2-cm centrifugal contactors.

Based on the results of the UREX+ demonstration with spent fuel demonstrated in the summer of 2003, the AMUSE code was modified to better model the TBP-nitric acid system at the high solvent loadings encountered in the UREX process. The changes to the code resulted in a much better model of the observed hydrogen stage profile [13].

An additional change to the code was required to model the co-extraction flowsheets. Because the nitric-acid concentration in the co-extraction feed is higher than required for UREX, and extraction of Zr increases at high nitrate activities, a more accurate prediction of the extraction behavior of Zr was necessary. Additionally, TcO_4^- extraction is greatly increased by the presence of Zr species in the organic phase. To account for this chemistry in the model, literature data were used to develop a new Zr D-value algorithm for UREX and PUREX, and a term for the Zr concentration in the organic phase was added to the Tc D-value algorithm. Figure 9 compares experimental data for D-values for Zr as a function of nitric acid concentration with the D-values calculated by the new equation in AMUSE.

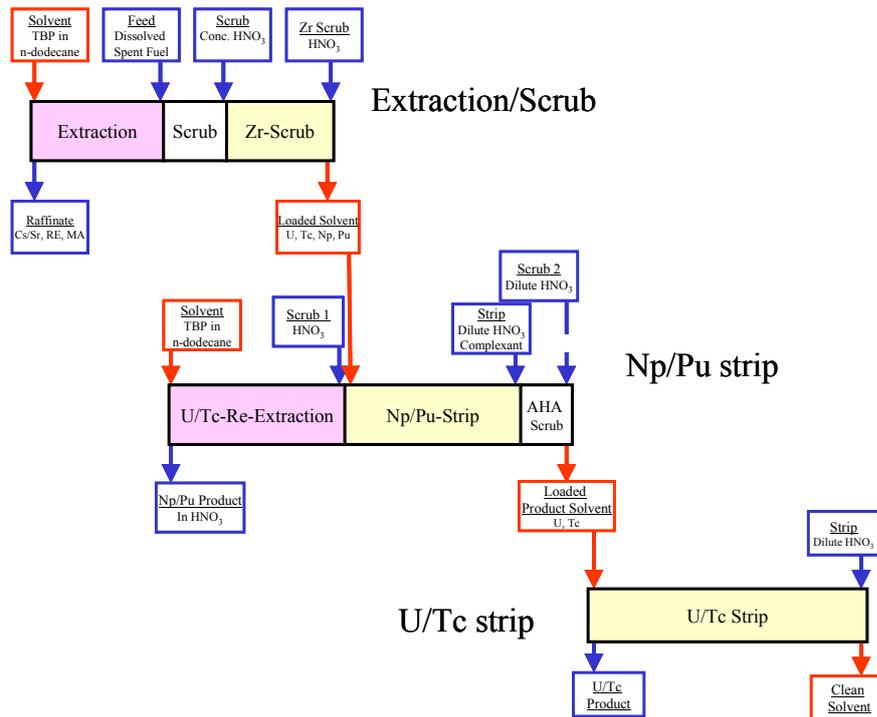


Figure 8. Process segments and streams for the Co-extraction of segment of UREX+2.

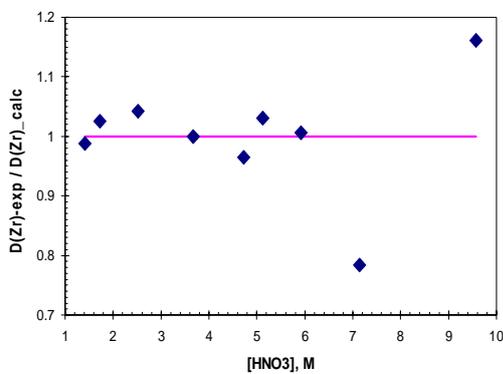


Figure 9. Experimental and calculated distribution ratio comparison for Zr as function of $[HNO_3]$.

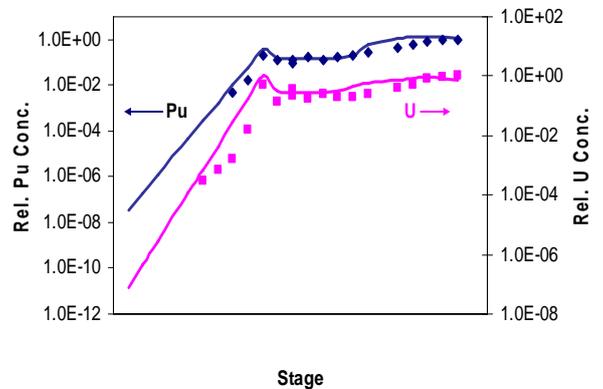


Figure 10. Aqueous stage profiles for Pu and U in the extraction/scrub section. Ex-perimental values shown as discrete points; AMUSE predictions shown as solid lines.

The UREX+2 co-extraction process was run with a dissolved spent fuel feed until steady state was achieved. At this point several samples of the effluents were collected and the process was shut down. In order to evaluate process performance and compare with AMUSE predictions, we collected stage samples of the organic and aqueous phases after shutdown of all of the process segments.

Shown in Figures 10 and 11 are the measured- and AMUSE- calculated aqueous stage profiles for plutonium and uranium in the Extraction/Scrub and Np/Pu-Strip sections. Figure 12 shows the uranium aqueous profile in the U/Tc-Strip section. All of the elemental concentrations are shown relative to maximum observed concentration in the experimental data except for Pu in the Np/Pu strip, where the first point was used as a reference. Concentrations that are below the detection limits of the analytical technique are not shown. As can be seen from the curves, the AMUSE predictions are generally very close to the observed behavior for these major species. The stage profiles of the UREX+2 process are generally well predicted by AMUSE, based on the results of the FY 2004 demonstration.

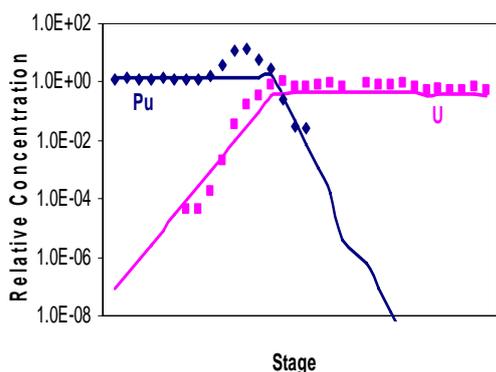


Figure 11. **Aqueous stage profiles for Pu and U in the Np/Pu-Strip section. Experimental values shown as discrete points; AMUSE predictions shown as solid lines.**

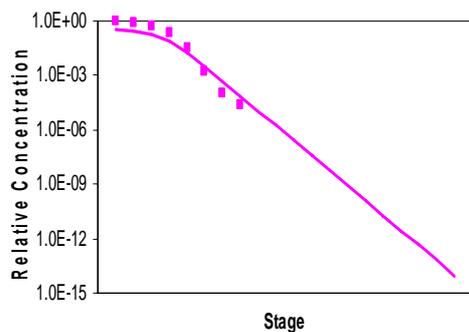


Figure 12. **Aqueous stage profiles for U in the U/Tc-Strip section. Experimental values shown as discrete points; AMUSE predictions shown as solid lines.**

Conclusions

The use of solvent extraction processes for spent fuel treatment has been proven to be a viable separation option for spent fuel partitioning and transmutation. Flowsheets developed using AMUSE have demonstrated the accuracy of the model predictions. The parallel development of the necessary process equipment, such as the ANL centrifugal contactor, further advances the practical implementation of solvent extraction. Additional work is planned to provide alternatives to the UREX+ process that will result in an economical and proliferation-resistant fuel cycle.

Acknowledgements

This work is supported by the U.S. Department of Energy, Office of Nuclear Energy, Science and Technology, under contract W-31-109-Eng-38.

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